Nuclear Science and Techniques **24** (2013) 040206

Mechanism of E' center induced by γ ray radiation in silica optical fiber material

LUO Wenyun[1,2] XIAO Zhongyin[1] WEN Jianxiang[1] YIN Jianchong[1] WU Wenkai[2]
CHEN Zhenyi[1] WANG Zihua[1] WANG Tingyun[1,*]

[1]*School of Communication and Information Engineering, Key Laboratory of Specialty Fiber Optics and Optical Access Networks, Shanghai University, Shanghai 200072, China*

[2]*School of Environmental and Chemical Engineering, Shanghai Applied Radiation Institute, Shanghai University, Shanghai 200444, China*

Abstract The characteristics of the best known defect centers E' in silica optical fiber material irradiated with γ ray were investigated by ESR at room temperature. A mechanism model of production of the E' center defect was established. The production of E' center includes two processes creation and activation. The strained bonds (or oxygen replacement) in silica networks lead to the creation of new defects whose concentration increases linearly with the dose. The pre-existing defects produce the activation, which tends to saturation. According to this model, the relation of E' center concentration changing with irradiation dose was obtained theoretically. The results are in good agreement with the experimental results.

Key words E' centers, γ ray radiation, Silica optical fiber material, ESR, Mechanism model

1 Introduction

In radiation environments, the characteristics of silica optical fibers are affected seriously because the radiation can induce defect centers in silica material, such as E' centers, non-bridging-oxygen hole centers, per-oxy radicals, and self-trapped holes. As the best known defect, E' center plays a major role in the radiation-induced transmission loss for silica optical fibers. Since R. A. Weeks[1] first reported the ESR spectrum of E' center in 1956, many works have been tried to understand the basic mechanisms of radiation-induced defect formation in silica glasses[1–11]. Recently, D. L. Griscom[2] gave a review about half a century of research on radiation-induced point defects in pure and doped glassy silica. Our previous works[12–17] discussed the influences of thermal annealing temperatures on irradiation induced E' centers in silica glass, and influences of irradiation on network microstructure, formation and conversion of defect centers of low water peak optical fiber. However, the mechanism of defect formation is not very clear until now. Therefore, it is essential to study defect center characteristics deeply, which is also helpful for improving the performance of material in radiation environment. F. R. Galeener *et al.*[18] have suggested a creation plus activation model to fit the experiment results of ESR signals in vitreous silica by X-rays from Cu-target tube. In our previous paper[16], we proposed a kinetic model for the radiation-induced production of the intrinsic point E' defect center. The relation of E' center concentration changing with dose was obtained theoretically.

In this paper, the characteristics of E' centers in silica optical fiber material irradiated with γ rays at room temperature are investigated and measured by using ESR. We obtain the relationship between the E' center concentration changing and irradiation doses accumulation by the experiments, which is in good agreement with the theoretical result. The mechanism of the radiation-induced E' center in optical fiber material has also been explained by these results.

Supported by National Program on Key Basic Research Project (973 Program, No.2012CB723405), Natural Science Foundation of China (No.60937003, 61077068, 61275090, 61275051, and 61027015) and Shanghai Natural Science Foundation (No.12ZR1411200)

* Corresponding author. *E-mail address*: tywang@mail.shu.edu.cn

Received date: 2013-02-28

2 Experimental

All samples in our experiments were made of high-purity silica, which produced by Shanghai Xinhu Glass, Inc., but sample of Group 1 and Group 2 were from two different batches. For ESR measurement, the samples are made into rods with a 2-mm diameter and a 2-cm length. The ESR spectra were obtained at room temperature on Varian E112 spectrometer (Shanghai Institute of Applied Physics, Chinese Academy of Sciences), operating at 9.53 GHz (X band), and employing a modulation field of 100-kHz frequency. All spectra of the same group samples were recorded on the same chart by changing only the amplifier gain. For Group 1, center magnetic field strength was 3412 Gauss, sweep range was 100 Gauss, response time constant was 0.25 s, and microwave power was 50 mW. In Fig.1(a), the amplifier gain was 1.25e3 for 50 kGy sample; and 5e4, for initial sample. For Group 2, center magnetic field strength was 3405 Gauss, sweep range is 50 Gauss, response time constant was 0.128 s, and microwave power was 50 mW. In Fig.1(b) the amplifier gain was 3.2e3. The intensities of the observed signals were normalized by the standard pitch signal. Samples were irradiated with γ rays from a ^{60}Co source at Shanghai Hexin Irradiation Factory. The irradiation doses are from 1 kGy to 50 kGy with a dose rate 2 kGy/h. The initial sample is not irradiated.

3 Results and discussion

The E' centers generated by γ ray irradiation come from pre-existing extrinsic defects and weakly bonding states of normal ≡Si-O-Si≡ bonds in silica glasses[11]. The pre-existing extrinsic E' center was an oxygen vacancy, which is related to the trapping of a hole at a neutral oxygen deficient center as expressed by Eq.(1). The other process of the E' center creation is the cleavage of a strained Si-O bond in silica glasses. The pair generation of E' centers and NBOHC's from intrinsic Si-O bonds occurs commonly in all the samples irradiated by γ rays. This mechanism model is expressed by Eq.(2). In addition, the strained Si-O bonds can become to pre-existing E' center by oxygen replacement, as expressed by Eq.(3).

$$\equiv\mathrm{Si–Si}\equiv + h\nu \rightarrow \equiv\mathrm{Si}\cdot + \mathrm{Si}^{+} + \mathrm{e}^{-} \quad (1)$$

$$\equiv\mathrm{Si–O–Si}\equiv + h\nu \rightarrow \equiv\mathrm{Si}\cdot + \cdot\mathrm{O–Si}\equiv \quad (2)$$

$$\equiv\mathrm{Si–O–Si}\equiv + h\nu \rightarrow \equiv\mathrm{Si–Si}\equiv + \mathrm{O} \quad (3)$$

The production of E' center includes two processes[16]: the creation of new defects, $N_C(D)$, and the activation of pre-existing defects, $N_A(D)$. The strained bonds (or oxygen replacement) in silica networks lead to the creation of new defects, and the pre-existing defects produce the activation. Therefore, the total defect concentration can be written as Eq.(4)[16].

$$N(D) = N_C(D) + N_A(D) = \frac{k_c k_p N_C}{k_c + k_p} D + \frac{k_c^2 N_C + k_c k_p N_p(0) + k_p^2 N_p(0)}{(k_c + k_p)(k_p + k_e)} \times \left[1 - e^{-(k_p + k_e)D}\right] \quad (4)$$

where k_c, k_p and k_e represent creation rate, activation rate and the rate of recombination of new defects, respectively. N_c and $N_p(0)$ are concentrations of the strained bonds and pre-existing defects. In Eq.(4), the first term on the right side is the process of defect creation, the concentration increases linearly with the dose. The second term shows the process of defect activation, which leads to defect concentration to tend to saturation. If k_c= 0, that is, without considering the creation of new defects, and

$$N(D) = \frac{k_p N_p(0)}{(k_p + k_e)}\left[1 - e^{-(k_p + k_e)D}\right] \quad (5)$$

The expression in Eq.(5) is the same as the Ref.[18]. Without considering the preexisting defects, $N_p(0)$ = 0, we can get from Eq.(4).

$$N(D) = \frac{k_c k_p N_C}{k_c + k_p} D + \frac{k_c^2 N_C}{(k_c + k_p)(k_p + k_e)} \times \left[1 - e^{-(k_p + k_e)D}\right] \quad (6)$$

We measured ESR spectra of the initial sample and irradiated samples at the room temperature. Fig.1 shows the ESR spectra of E' centers of Group 1 and Group 2 samples before and after 50 kGy irradiation. It can be seen that the ESR spectra have the same g value as the E' center characterized by g = 2.0006. Therefore, the observable ESR signal is attributed to E' color centers.

The initial sample of Group 1 has a weak signal of E' center before irradiation (Fig.1(a)), but the initial sample of Group 2 has not any ESR signals

(Fig.1(b)), indicating that the structure of samples of Group 2 is more stable than Group 1.

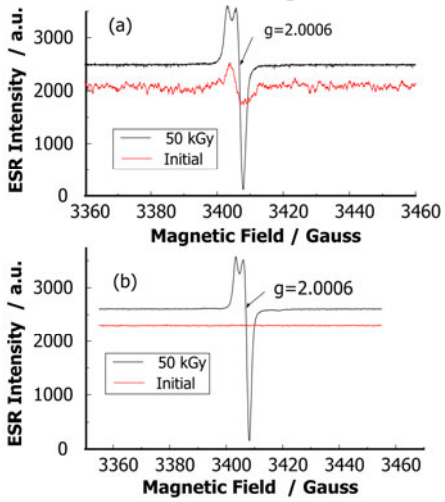

Fig.1 ESR spectra of E' centers irradiated with 50 kGy and the initial one. (a) Group 1, (b) Group 2.

According to a double integration of the derivative spectra, the E' concentrations with different irradiated doses are calculated (Fig.2). Based on these experimental results, the parameters k_c, k_p, k_e and N_c, N_p used in Eq.(4) of the above theoretical model are determined, which are shown in Table 1. Fig.2 shows that the E' center concentrations change with doses for Group 1 and Group 2. The E' center concentrations increase with irradiated doses obviously, and the simulated and experimental results have a good agreement for either Group 1 or Group 2. Moreover, this increase shows nearly linear trend for Group 1 (Fig.2(a)), and nonlinear trend for Group 2 (Fig.2(b)) in the dose range from 0 to 60 kGy.

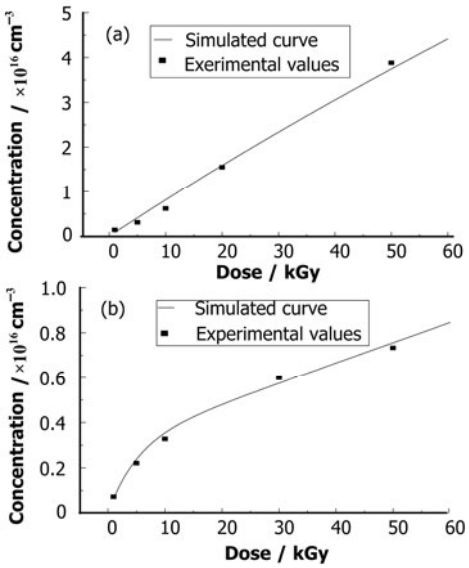

Fig.2 Simulated and experimental results of E' center concentrations changing with doses. (a) Group 1, (b) Group 2.

Table 1 Parameters used in simulation

	$N_p(0)$/cm^{-3}	N_c /cm^{-3}	k_c /cm^2·kGy^{-1}	k_p / cm^2·kGy^{-1}	k_e / cm^2·kGy^{-1}
Group 1	1.84×10^{15}	3.20×10^{17}	2.58×10^{-3}	3.8×10^{-3}	8.0×10^{-3}
Group 2	1.84×10^{14}	2.72×10^{17}	2.58×10^{-3}	3.8×10^{-4}	2.0×10^{-1}

The simulated curve can be analyzed by Eq.(4). Fig.3(a) shows that the number of creative E' center $N_C(D)$ increases faster than the activated E' center $N_A(D)$, and the combined E' center concentration $N(D)$ increases linearly with radiation doses, indicating that the creation of new defects is the main process for Group 1 in this dose range. In Fig.3(b), the number of activated E' center $N_A(D)$ increases rapidly at low doses (D<20 kGy), then tends to saturation; the number of creative E' center $N_C(D)$ keeps linear increasing in the whole dose range. It indicates that all pre-existing defects in the first process were activated, thus accounting for the initial nonlinear region of combined $N(D)$ curves; in the second process, the strained bonds were ruptured to generate new E' center defects while activated E' center became saturation, thereby accounting for the linear portion of $N(D)$ curves at higher doses (D > 20 kGy) for Group 2.

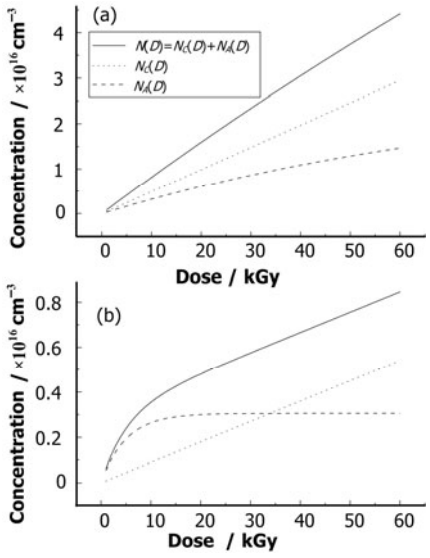

Fig.3 Simulated curve by theoretical model. (a) Group 1, (b) Group 2.

The above theoretical model is called as activation plus creation model[18], whose mathematical expression is very simple as Eq.(4). The important parameters were determined as follows: N_c, the concentration of the strained bonds, $N_p(0)$, the concentration of pre-existing defects, k_c, k_p and k_e, the rate to create new defects, the rate to activate pre-existing defects and the rate of recombination of new defects. All determined parameters used in simulation are listed in Table 1. It can be found that in the samples of Group 1, there are more pre-existing defects and more strained Si-O bonds than Group 2. So the samples' structure of Group 2 is more stable than Group 1, which also can be seen from ESR signals of the initial samples in Fig.1. The rate of activation of pre-existing defects is greater in the samples of Group 1, while the rate of recombination of new defects is smaller than Group 2. Although the rate of creation of new E' centers is the same in two groups, the number of strained bonds in Group 1 is more than in Group 2. For Group 1, creation is the main process; for Group 2, activation dominates at low doses, and creation dominates at high doses.

Although the samples of Group 1 and Group 2 are made of high-purity silica, and produced by the same company, there is still very small difference in the microstructure for different bitches. The above theoretical analysis shows that the samples of Group 2 have more stable microstructure than Group 1 since they have fewer pre-existing defects and strained bonds. So the radiation hardness of Group 2 is better than that of Group 1.

4 Conclusion

We investigated characteristics of the E' defect centers in silica optical fiber material irradiated with γ ray by ESR at room temperature, proposing its mechanism model. In creation process, the strained bonds in silica networks lead to the new defects whose concentration increases linearly with the dose. In activation process, the pre-existing defects produce the activation tending to saturation. A simple formula is given by the mechanism model to simulate the relation of E' center concentration changing with dose. For Group 1, the creation of new defects is the main process, E' center concentration increases linearly with the radiation doses. For Group 2, activation dominates at low doses; and creation, at high doses, so E' center concentration increases nonlinearly at first, then linearly with radiation doses. The simulated results are in good agreement with the experimental ones. This theoretical analysis is simple, and can fit experimental results by adjusting simulation parameters for each kind of samples. The structure information of samples can be inferred from the determined parameters. The creation plus activation model can separate the two processes.

References

1 Weeks R A. J Appl Phys, 1956, **27:** 1376–1381.

2 Griscom D L. J Non-Cryst Solids, 2011, **357:** 1945–1962.

3 Griscom D L, Levy P. In proc. radiation effects of optical materials, The Society of Photo-optical Instrumentation Engineers Confer, Bellingham, WA, 1985, 541, 38–59.

4 Griscom D L, Galeener F L, Weber M J. In Proc. Defects in Glasses Symp, Pittsburgh, PA, 1986, 213–221.

5 Zatsepin A F. J Non-Cryst Solid, 2011, **357:** 1856–1859.

6 Skuja L. J Non-Cryst Solid, 1998, **239:** 16–48.

7 Saito K, Ikushima A J. J Appl Phys, 2002, **91:** 4886–4890.

8 Devine R A B, Arndt J. Phys Rev B, 1989, **39:** 5132–5138.

9 Agnello S, Nuccio L. Phys Rev B, 2006, **73:** 115203.

10 Friebele E J, Griscom D L, Marrone M J. J Non-Cryst Solid, 1985, **71:** 133–144.

11 Imai H, Arai K, Isoya J, *et al.* Phys Rev B, 1993, **48:** 3116–3123.

12 Wang T Y, Xiao Z Y, Luo W Y. IEEE Trans Nucl Sci, 2008, **55:** 2685–2688.

13 Wen J X, Luo W Y, Xiao Z Y, *et al.* J Appl Phys, 2010, **107:** 044904.

14 Wang T Y, Wen J X, Luo W Y, *et al.* J Non-Cryst Solid, 2010, **356:** 1332–1336.

15 Xiao Z Y, Luo W Y, Wang T Y. Acta Phys Sin, 2007, **56:** 2731–2735 (in Chinese).

16 Xiao Z Y, Wang T Y, Luo W Y, *et al.* Acta Phys Sin, 2008, **57:** 2273–2277(in Chinese).

17 Wen J X, Peng G D, Luo W Y, *et al.* Opt Express, 2011, **19:** 23271–23278.

18 Galeener F L, Kerwin D B, Miller A J. Phy Rev B, 1993, **47:** 7760–7779.